Rare Metal Materials and Engineering
Volume 47, Issue 4, April 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2018, 47(4): 1096-1099.

ARTICLE

Phase Transformation Kinetics of Cu-Be-Co-Zr Alloy During Aging Treatment

Zhou Yanjun[1], Song Kexing[1], Mi Xujun[2], Liu Yong[1], Yang Shaodan[1], Li Zhou[3]

[1] Henan University of Science and Technology, Luoyang 471023, China; [2] General Research Institute for Nonferrous Metals, Beijing 100088, China; [3] Central South University, Changsha 410006, China

Abstract: The phase transformation kinetics of Cu-Be-Co-Zr alloy during aging treatment was investigated. Based on the relationship between electrical conductivity and volume fraction of precipitates, the phase transformation ratios of Cu-Be-Co-Zr alloy aged at 480 °C for different holding time (0, 30, 60, 120, 180, 240, 360, 480, and 600 min) were calculated. The kinetics equation of phase transformation and the electrical conductivity equation were derived. The isothermal transformation kinetics S-curves of Cu-Be-Co-Zr alloy was drawn. By the integral equation of solid thermal decomposition reaction mechanism, the phase transformation mechanism of Cu-Be-Co-Zr alloy is controlled by three dimensions of diffusion.

Key words: Cu-Be-Co-Zr alloy; aging; electrical conductivity; phase transformation kinetics

Due to high strength and hardness, good electrical and thermal conductivity, and low elastic modulus, Cu-Be-Co-Zr alloys are widely used in the key components of aerospace, oceaneering and petroleum industry etc.[1-3]. The formability of Cu-Be-Co-Zr alloys is raised by solution treatment and their strength and hardness are improved significantly by the subsequent aging treatment[4,5]. After solution treatment, the solute atoms are fully dissolved in the Cu-matrix and the α supersaturated solid solution is formed by rapid cooling. During subsequent aging process, a series of phases are precipitated from α supersaturated solid solution[6,7]. The electrical conductivity is sensitive to the formation of precipitates. So the phase transformation behavior can be studied by analyzing the change of electrical conductivity and precipitates during aging[8-10].

Currently, the phase transformation behavior of Cu-Cr, Cu-Cr-Zr, Cu-Al-Be, Cu-Al-Ni, Cu-Ni-Si, Mg-Nd-Zn, Ti-Mo-Al-Nb, and Ni-Cr-Mo alloys are extensively investigated by researchers, and the structure of precipitates are analyzed in detail as well[8,11-17]. For high-strength and high-conductivity Cu-Co-Be-(Zr) alloys, a large number of studies mainly focus on the preparation, aging treatment, properties (mechanical, electrical, thermal, tribological etc.), and microstructures[2-5,18-21]. For instance, Tang et al. investigated the effect of normal aging (NA) and interrupted aging (IA) on the mechanical properties of a Cu-Be-Co-Ni alloy by tensile and Kahn tear tests[18]. It is confirmed that the uniform elongation and plane stress fracture toughness are improved significantly by IA process with tiny decrease in ultimate tensile strength. The fracture surface of samples treated by NA and IA process is intergranular fracture and transgranular fracture, respectively. However, the phase transformation kinetics and mechanism of Cu-Co-Be alloys during aging process have not been clarified yet. There are seldom reports about the kinetics equation of precipitates transformation, especially for the high conductivity Cu-Be-Co-Zr alloy. Therefore, the objective of this study is to focus on the phase transformation kinetics and mechanism of Cu-Be-Co-Zr alloy during aging process based on the relationship between electrical conductivity and volume fraction of precipitates.

Received date: April 15, 2017
Foundation item: National Key Research and Development Program of China (2016YFB0301400); State Key Program of National Natural Science Foundation of China (U1502274); Innovation Scientists and Technicians Troop Construction Projects of Henan Province (C20150014); Program for Innovation Research Team (in Science and Technology) in University of Henan Province (14IRTSTHN007)
Corresponding author: Song Kexing, Ph. D., Professor, School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang 471023, P. R. China, Tel: 0086-379-64231912, E-mail: kxsong@haust.edu.cn

1 Experiment

The Cu-Be-Co-Zr ingot was prepared by a ZGJL0.01-40-4 vacuum induction furnace. The raw materials were electrolytic copper (99.99 wt%, purity), Cu-3.3wt%Be master alloy, Cu-40wt%Zr master alloy, and Co flake (99.95 wt%, purity). The melting temperature range was from 1150 °C to 1250 °C. The molten metals were poured into a metallic mould of cast iron to obtain an ingot with a diameter of 100 mm. The alloy consisted of 0.48 wt% beryllium, 0.94 wt% cobalt, 0.31 wt% zirconium and balance of copper by chemical analysis. After subsequent thermal extrusion and cold rolling, a plate with a cross-section of 15 mm×5 mm was got. Then, the specimens were solution treated at 950 °C for 60 min and then quenched in water, followed by aging at 480 °C and holding for 30, 60, 120, 180, 240, 360, 480, 600 min, and cooled in air.

The electrical conductivity was measured using a Sigma 2008 B/C Digital Eddy Current Metal Conductivity Tester according to the standard ASTM E1004-02 with the name of "Standard Practice for Determining Electrical Conductivity Using the Electromagnetic (Eddy-Current) Method". The measuring range of this instrument is from 0.8 %IACS to 110 %IACS with an accuracy of about ±0.5 %IACS (International Annealed Copper Standard).

2 Results and Discussion

2.1 Electrical conductivity of Cu-Be-Co-Zr alloy

The effect of aging time at 480 °C on electrical conductivity of Cu-Be-Co-Zr alloy is shown in Fig.1. The electrical conductivity of Cu-Be-Co-Zr alloy in solution state is 24.6 %IACS. After aging for 60 min, the electrical conductivity increases remarkably to 40.2 %IACS. With the prolonging of aging time (60 min to 600 min), the electrical conductivity increases gradually and has a peak value of 43.8 %IACS after aging for 480 min. The electrical conductivity of Cu-Be-Co-Zr alloy is closely related to the solute atoms in Cu-matrix and the integrity of the Cu-matrix lattice. The ordering of solid solution is in favour of improving the integrity of matrix lattice, and reducing the scattering of electron[22]. At the initial stage of aging (0~60 min), the precipitates continually form from the Cu-matrix. The integrity of Cu-matrix lattice recovers gradually and the electronic conduction channel becomes unobstructed, which results in the significant increase of electrical conductivity (Fig.1).

2.2 Phase transformation kinetics of Cu-Be-Co-Zr alloy

The supersaturated α phase forms after solution treatment, and then a series of precipitates distribute on the Cu-matrix during the subsequent aging treatment. The transformation ratio φ of precipitates can be defined as follows:

$$\varphi = \frac{V}{V_e} \quad (1)$$

where, V_e is the equilibrium volume of precipitates per unit volume in matrix at equilibrium state, V is the volume of precipitates formed per unit volume in matrix at a certain time (t). Prior to phase transformation (i. e. solution state), V=0 and φ=0. When the precipitates no longer form or the electrical conductivity no longer increases (i. e. equilibrium state), $V=V_e$ and φ=1.

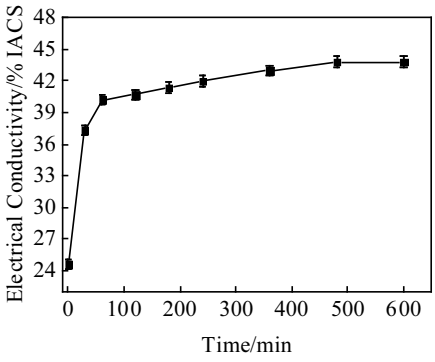

Fig.1 Electrical conductivity of Cu-Be-Co-Zr alloy as a function of aging time at 480 °C

The electrical conductivity is sensitive to the formation of precipitates[8]. The relationship between electrical conductivity and volume fraction of precipitates is linearity, as shown in Eq.(2).

$$\gamma = \gamma_0 + A\varphi \quad (2)$$

The initial electrical conductivity (γ_0) is 24.6 %IACS (Fig.1). After aging for 480 and 600 min, the electrical conductivity has a peak value of 43.8 %IACS (γ_{min}). It can be assumed that the equilibrium state of precipitation has achieved at this moment (φ=1). So the coefficient $A=\gamma_{max}-\gamma_0$ and the value is 19.2 %IACS. According to the experimental data of electrical conductivity (γ), the transformation ratio (φ) of precipitates corresponding to aging time are calculated, as shown in Table 1.

In addition, the relationship between transformation ratio (φ) of precipitates and aging time follows the Avrami empirical formula[8-10]:

$$\varphi=1-\exp(-bt^n) \quad (3)$$

where b and n are constant factors. The coefficient b depends on transition temperature, initial composition, and grain size of precipitates. The coefficient n depends on the types of phase transition and nucleation position.

Take logarithm two times on both sides of Eq.(3):

$$\ln[\ln(1/(1-\varphi))]=n\ln t+\ln b \quad (4)$$

The $\ln[\ln(1/(1-\varphi))]$-$\ln t$ fitting curve is obtained by substituting the values of φ and t in Table 1 into Eq.(4), as observed in Fig.2. Fig.2 shows that $\ln[\ln(1/(1-\varphi))]$ and $\ln t$ is

Table 1 Electrical conductivity (γ) and transformation ratio of precipitates (φ) corresponding to aging time (t)

t/min	0	30	60	120	180	240	360	480	600
γ/%IACS	24.6	37.3	40.2	40.7	41.4	42.0	43.0	43.8	43.8
φ	0.00	0.66	0.81	0.84	0.88	0.91	0.96	1.00	1.00

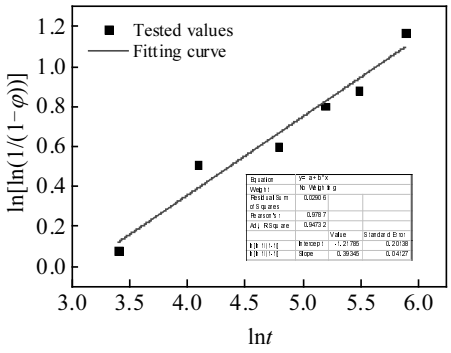

Fig.2 ln[ln(1/(1–φ))]-ln$t$ fitting curve of Cu-Be-Co-Zr alloy

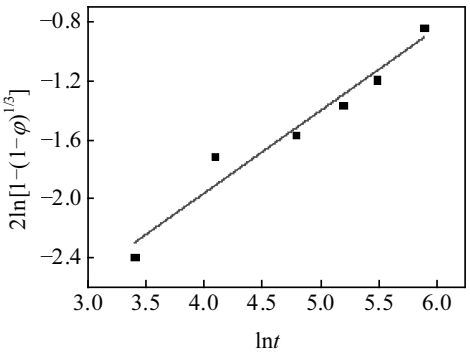

Fig.4 $2\ln[1-(1-\varphi)^{1/3}]$-ln$t$ fitting curve of Cu-Be-Co-Zr alloy aging at 480 °C

in accordance with the linear relationship. So n is the slope of line, n=0.3935, and ln$b$ is the intercept, ln$b$=−1.2179, and thus, b=0.2959. Therefore, the phase transformation kinetics equation of Cu-Be-Co-Zr alloy aging at 480 °C is described as:

$$\varphi = 1-\exp(-0.2959t^{0.3935}) \quad (5)$$

Fig.3 is the transformation kinetics S-curves of Cu-Be-Co-Zr alloy according to Eq. (5). Fig.3 shows that the transformation speed is slower during initial aging state, then it becomes faster with the increasing of aging time, and the speed is gradually slower at the end of aging. In addition, the tested values coincide well with the theoretic data.

Furthermore, the electrical conductivity equation of Cu-Be-Co-Zr alloy aged at 480 °C is derived by substituting Eq. (5) into Eq. (2). The calculation values of electrical conductivity according to Eq. (6) fit well with the experimental results.

$$\gamma = 24.6+19.2[1-\exp(-0.2959t^{0.3935})] \quad (6)$$

2.3 Phase transformation mechanism of Cu-Be-Co-Zr alloy

The integral kinetics function of three dimension diffusion is described as:

$$[1-(1-\varphi)^{1/3}]^2 = A\exp[-E/(RT)]t \quad (7)$$

where, $k = A\exp[-E/(RT)]t$ is a constant. Take logarithm on both sides of Eq.(7):

$$2\ln[1-(1-\varphi)^{1/3}] = \ln t + \ln k \quad (8)$$

The $2\ln[1-(1-\varphi)^{1/3}]$-ln$t$ fitting curve is obtained by substituting the values of φ and t (Table 1) into Eq. (8), as shown in Fig.4. Fig.4 shows that $2\ln[1-(1-\varphi)^{1/3}]$ and ln$t$ is in accordance with the linear relationship. The slope of $2\ln[1-(1-\varphi)^{1/3}]$-ln$t$ fitting curve is in close proximity to the value of n (1). So the phase transformation mechanism of Cu-Be-Co-Zr alloy aging at 480 °C is controlled by three dimension diffusion.

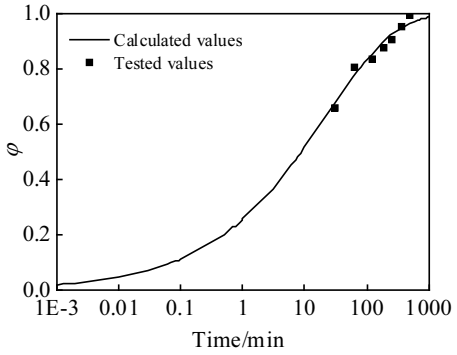

Fig.3 Transformation kinetics S-curves of Cu-Be-Co-Zr alloy

3 Conclusions

1) The electrical conductivity of Cu-Be-Co-Zr alloy has an obvious variation with aging time. The transformation ratio of precipitates is sensitive to the electrical conductivity of Cu-Be-Co-Zr alloy.

2) The phase transformation kinetics equation, and the electrical conductivity equation of Cu-Be-Co-Zr alloy aged at 480 °C are described as $\varphi = 1-\exp(-0.2959t^{0.3935})$, and $\gamma = 24.6+19.2[1-\exp(-0.2959t^{0.3935})]$, respectively.

3) The phase transformation mechanism of Cu-Be-Co-Zr alloy aged at 480 °C is controlled by three dimension of diffusion.

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Cu-Be-Co-Zr 合金时效析出动力学

周延军[1]，宋克兴[1]，米绪军[2]，刘　勇[1]，杨少丹[1]，李　周[3]
(1. 河南科技大学，河南 洛阳 471023)
(2. 北京有色金属研究总院，北京 100088)
(3. 中南大学，湖南 长沙 410006)

摘　要：研究了 Cu-Be-Co-Zr 合金 480 ℃恒温时效条件下的时效析出动力学。根据导电率与析出相体积分数的关系，计算了 Cu-Be-Co-Zr 合金不同时效时间（0, 30, 60, 120, 180, 240, 360, 480, 600 min）对应的析出相转变比率，建立了 Cu-Be-Co-Zr 合金 480 ℃时效条件下的析出相变动力学方程和导电率方程，并在此基础上绘制了等温转变动力学 S 曲线；采用固态热分解反应机理的积分方程，揭示了 Cu-Be-Co-Zr 合金时效析出转变机制为受扩散控制的反应机理。

关键词：Cu-Be-Co-Zr合金；时效；导电率；相变动力学

作者简介：周延军，男，1985 年生，博士，河南科技大学材料科学与工程学院，河南 洛阳 471023，电话：0379-64231269，E-mail: dazhou456@163.com